

State of California

AIR RESOURCES BOARD

METAM SODIUM APPLICATION MONITORING REPORT

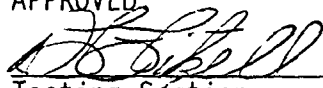
Ambient Air Monitoring in Contra Costa County during
March 1993 after an Application of Metam Sodium to a Field

Engineering Evaluation Branch
Monitoring and Laboratory Division

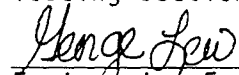
Test Report No. C92-070A

Report Date: July 14, 1993

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This report has been reviewed by the staff of the Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Metam Sodium Monitoring in Contra Costa County during March 1993

This report presents the results of ambient air monitoring after a ground injection application of metam sodium at a selected field in Contra Costa County. The effects of the metam sodium application were determined by measuring the amounts of methyl isothiocyanate (MITC), the primary breakdown product, which has pesticidal activity, acts as a fumigant, and is found in the air. The concentrations determined ranged from 0.051 ug/m³ (0.017 ppbv) to 242 ug/m³ (81.0 ppbv). The results are based on samples collected by the Air Resources Board Monitoring and Laboratory Division staff and analyzed by the Air and Industrial Hygiene Laboratory staff. The results have been reviewed by the ARB staff and are believed to be accurate within the limits of the methods.

Acknowledgments

Jack Rogers and LaJuan Taylor were the Instrument Technicians. Pat McKenzie of Ronald Nunn Farms assisted in arranging for a suitable field to monitor. Assistance was provided by Lynn Baker and Ruth Tomlin of the ARB's Toxic Air Contaminant Identification Branch. Chemical analyses were performed by the Air and Industrial Hygiene Laboratory. Confirmation analysis was performed by the California Department of Food and Agriculture laboratory in Sacramento, CA.

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State of California
Air Resources Board

Metam Sodium Monitoring in Contra Costa County

I. INTRODUCTION

The Air Resources Board (ARB) Engineering Evaluation Branch (EEB) conducted a three-day source impacted ambient monitoring program for an application of metam sodium in Contra Costa County during the month-of March 1993. This monitoring was performed at the request of the Office of Environmental Health Hazard Assessment (OEHHA), the California Department of Pesticide Regulation (DPR), and the ARB Toxic Air Contaminant Identification Branch (TACIB). The effects of the metam sodium application were determined by measuring the amounts of methyl isothiocyanate (MITC), the primary breakdown product, which has pesticidal activity, acts as a fumigant and is found in the air.

The purpose of this monitoring program was twofold: 1) to obtain data when MITC emissions were expected to be lowest under conditions with cool air and cool soil temperatures as well as soil injection of metam sodium, instead of application by introduction through a sprinkler irrigation system (sprinkler irrigation application) and 2) to establish the reliability of the analytical laboratory to determine low levels of this compound. Monitoring for carbon disulfide did not occur because of the above reasons, as well as the fact that another laboratory would be required to conduct the analysis.

This was preparatory to a "worst case" (warm air, warm soil temperatures and sprinkler irrigation application) monitoring program planned for the summer of 1993. It is anticipated that monitoring for carbon disulfide will occur after this application.

The Pesticide Use Report for 1991 indicates metam sodium is most widely used (1,395,942 pounds) prior to planting carrots. Heaviest use appears to be August through December in Kern County.

II. DESCRIPTION

Metam sodium (molecular weight 129.18 g/mole) is a soil fumigant used as a fungicide, herbicide, insecticide and nematocide. It has an unpleasant odor, similar to that of carbon disulfide. It is soluble in water (72.2 g/100 ml), moderately soluble in alcohol and sparingly soluble in other solvents. It is applied by soil injection or sprinkler injection. It rapidly breaks down in the presence of water

into methyl isothiocyanate (MITC), which has pesticidal activity. Metam sodium is not regulated as a restricted use material under section 6400, Title 3 of the California Code of Regulations.

MITC is a crystalline substance (m.p. 35-36°C, b.p. 119°C) with a molecular weight of 73.12. It is slightly soluble in water and freely soluble in alcohol and ether (Merck Index, Eleventh Edition, 1989).

Lethality values for MITC range from 29 mg/m³ (LC₁₀₀, rat 30-minute exposure) to 1900 mg/m³ (LC₅₀, rat 1-hour exposure) (OEHHA, 1992). The most sensitive toxicity end point, eye irritation, was reported in cats exposed to 0.2 mg/m³ MITC for 4 hours. Based on that study, OEHHA set a 24-hour action level for eye irritation of 0.1 ppb. Studies are underway to refine the odor threshold and eye irritation levels for humans.

III. SAMPLING LOCATIONS

A field of about 95 acres was selected (FIGURE I) by Pat McKenzie of Ron Nunn Farms Co. and approved by ARB staff to use for application monitoring. The prevailing wind in the area is from the northwest. Three samplers were set up: one approximately 15 yards from the northern perimeter and two approximately 15 yards from the southern perimeter of the field. A meteorological station was set up near one of the downwind samplers (SE), see FIGURE II.

IV. SAMPLING METHODOLOGY

The sampling method used during this study required passing measured quantities of ambient air through charcoal tubes. These tubes are 8 mm x 110 mm, with 400 mg in the primary section and 200 mg in the secondary (SKC catalog #226-09). Any MITC present in the sampled ambient air is captured by the charcoal adsorbent contained in the tubes. Subsequent to sampling, the tubes were transported in an iced container to the Air and Industrial Hygiene Laboratory (AIHL) in Berkeley for analysis.

Sampling trains designed to operate continuously were set up at the three sampling sites identified in FIGURE II. Duplicate samples were obtained from all three sites. The application took much longer than most monitored by EEB staff and occurred only during daylight hours. For these reasons, the sampling schedule outlined in the QA Plan (APPENDIX I, Attachment D) was not followed. Sample tubes were changed before application began in the morning, once during the application period and after application ended for the day.

Each sample train consisted of an charcoal tube with tube cover, Teflon fittings and tubing, rain shield, flow meter, train support, and a

12VDC battery-powered vacuum pump. A diagram of the sampling train is shown in FIGURE III. Each tube was prepared for use by breaking off each sealed glass end and then immediately inserting the tube into a Teflon fitting. The tubes were oriented in the sampling train according to a small arrow printed on the side of each tube indicating the direction of flow. Covers were placed around the tube to protect the adsorbent from exposure to sunlight.

The sample pump was started and the flow through a rotometer adjusted with a metering valve to an indicated reading of 2.0 liters per minute (lpm). A leak check was performed by blocking off the sample inlet. The sampling train would be determined to be leak-free, if the indicated flow dropped to zero. Upon completion of a successful leak check, the indicated flow rate was again set at 2.0 lpm and was recorded (if different from the planned 2.0 lpm) along with date, time, and site location. Calibration prior to use in the field indicated that an average flow rate of 1.92 lpm was actually achieved when the rotometers were set to 2.0 lpm. This average flow rate was used to calculate all sample volumes.

At the end of each sampling period the final indicated flow rate (if different than the set 2.0 lpm), the stop date and time were recorded. The charcoal tubes were then removed from the sample train, end caps installed on both ends, and identification labels affixed to each tube. Each tube was then placed in a culture tube with a screw cap and stored with ice in a covered chest until the tubes were delivered to the laboratory for analysis.

V. ANALYTICAL METHODOLOGY

The charcoal tubes recovered from each sampler were analyzed by the AIHL staff. The charcoal in the primary and secondary section of each sample tube was extracted with carbon disulfide followed by gas chromatography (GC) separation on a DB-624 capillary column and measurement by a nitrogen/phosphorous detector (NPD), see APPENDIX I, Attachment E. Confirmation was performed on the already extracted samples by AIHL staff using gas chromatography/mass spectroscopy (GC/MS). The California Department of Food and Agriculture (CDFA) laboratory used GC/NPD for analysis of some of the duplicate charcoal tube samples (TABLE IV).

The Jerome analyzer is a hand held instrument that determines levels of hydrogen sulfide based on the reaction of that compound with a gold film surface. The change of electrical conductivity across the gold film due to this reaction is proportional to the hydrogen sulfide concentration. The lowest detectable level is 3 parts per billion by volume (ppbv).

VI. RESULTS

The application was by tractor and took about three days. Application occurred only during daylight hours. It was applied at a rate of 18 gal/acre and the formulation contained 32.7% active ingredient (metam sodium). The application was set for a depth of 8 inches in soil that would be characterized as clay and loam. Following the application, no soil sealing was used to mitigate possible air emissions. The PCA recommendation is included as APPENDIX II.

The monitoring results are shown in TABLE I. A summary of the on site meteorological data is presented in TABLE II. Additional detailed meteorological data from the California Irrigation Management Information System (CIMIS) station, located in Brentwood, is presented in APPENDIX III. A summary of the monitoring and meteorological data is presented in TABLE III. The Quality Assurance confirmation data is shown in TABLE IV.

The ground application continued throughout the monitoring period. TABLE III is an attempt to graphically correlate the wind speed and direction, the application pattern and the values detected. The area covered with the cross-hatch represents the portion of the field that was applied during the indicated sampling period. The diagonal lines represent the cumulative total portion of the field that had been applied prior to the start of that sampling period. As TABLE I. shows, significant levels of MITG were found. Values ranged from 0.051 ug/m³ (0.017 ppbv) to 242. ug/m³ (81.0 ppbv).

At the beginning of the application a Jerome hydrogen sulfide (H₂S) analyzer was used to measure ambient values (calibration data, APPENDIX IV). Downwind of the application (15 to 25 yards), values did not exceed 8 ppb. Measuring the levels directly above the ground (approx. 4 inches) shortly after injection yielded values of about 8 ppb. At the beginning of the application, a pesticide spill resulted from plugged lines on the tractor. Monitoring the air directly over this surface spill, the maximum concentration was 40 ppb.

VII. QUALITY ASSURANCE

Reproducibility, linearity, collection and extraction efficiency, minimum detection limit and storage stability are described in the S.O.P. for metam sodium (APPENDIX I, Attachment E).

All of the procedures outlined in the metam sodium Quality Assurance Plan (APPENDIX I, Attachment D) were followed. Spikes were prepared by the AIHL. Spikes SP-11 and SP-12 were stored overnight at the application site, spikes SP-13 and SP-14 were stored in an ice chest overnight. The results are included in TABLE I. The recovery levels for the 1 ug/tube spikes ranged from 68 to 72%. In addition,

confirmation for the levels of selected field samples was completed by other AIHL staff using GC/MS and by CDFA staff using GC/NPD. The results for GC/MS ranged from 83-123% of the values determined by AIHL using GC/NPD. The values determined by CDFA also using GC/NPD ranged from 93-126% of the values found by AIHL using GC/NPD (TABLE III). Extensive QA/QC work was conducted prior to the monitoring program and is presented in APPENDIX V.

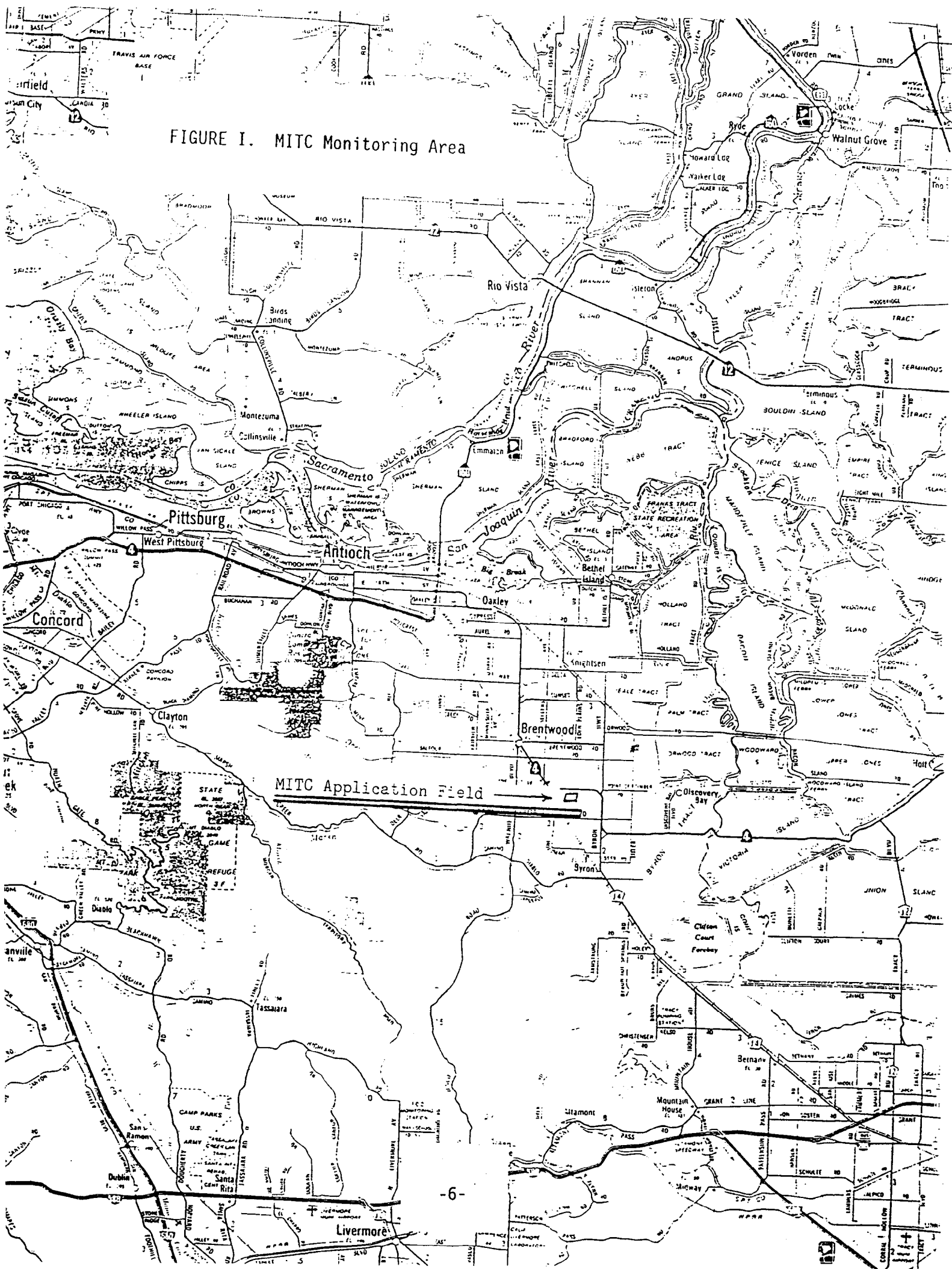
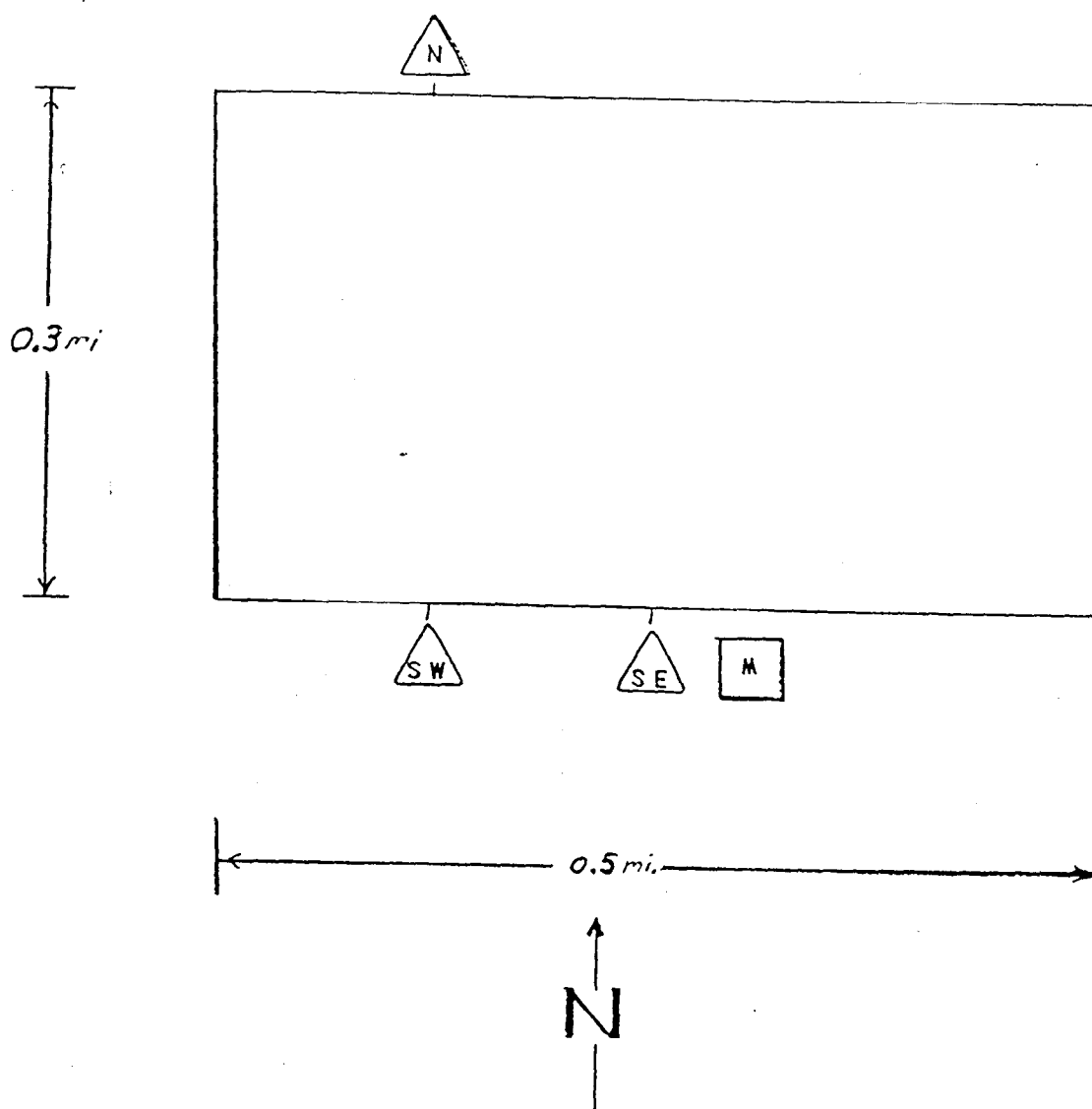


FIGURE I. MITC Monitoring Area

FIGURE II. MITC Monitoring Sites





Legend	
	Sampling station
	Met. station

FIGURE III. Monitoring Apparatus

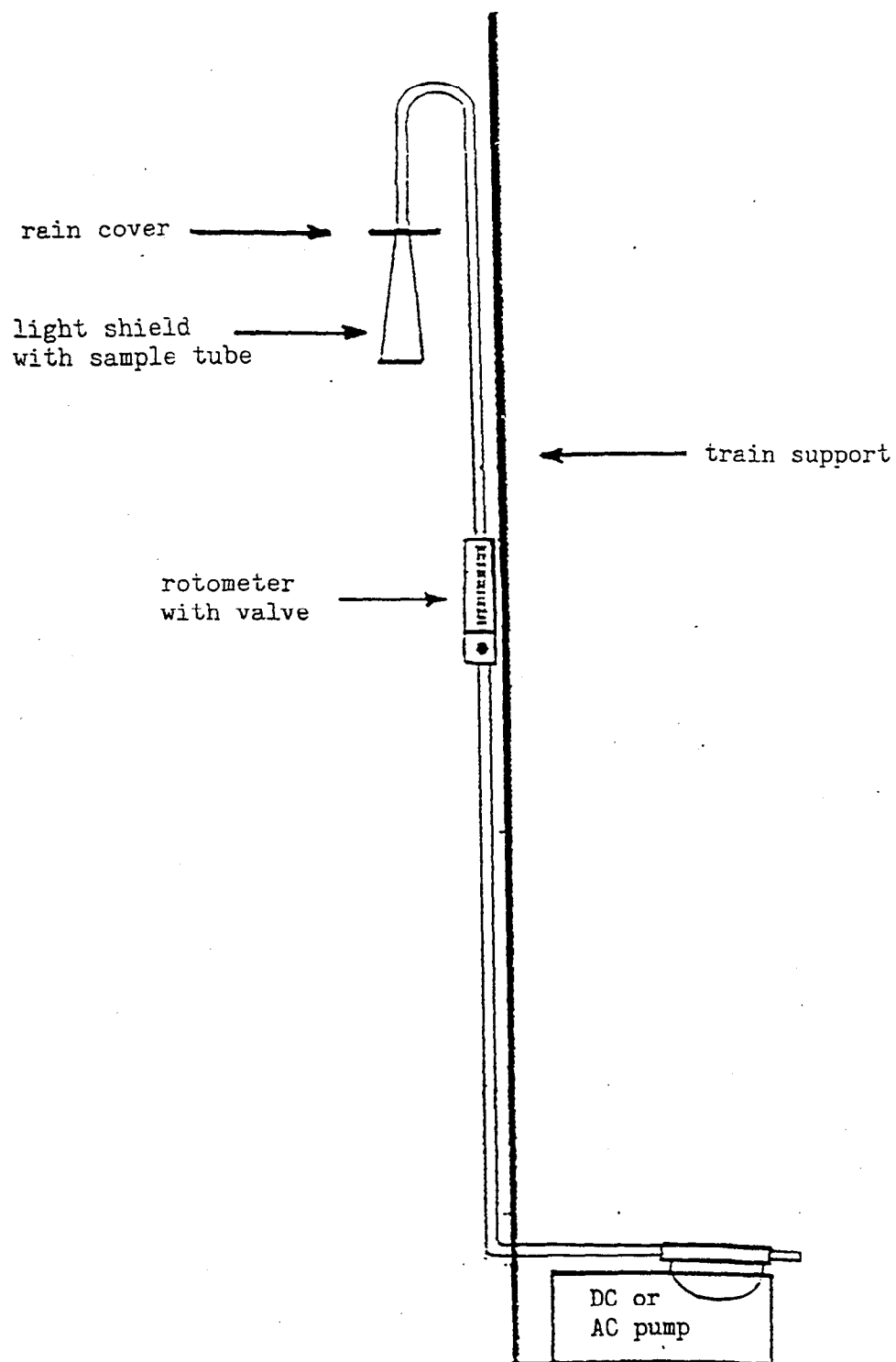


TABLE I. MITC Monitoring Data

Sample ID	Time (min.)	Volume* (m ³)	Total (ug)	Concentration (ug/m ³)	(ppbv)	Date (Approx. time)
N-0	135	0.259	ND	--	--	Background
SE-0	115	0.221	ND	--	--	3/8/93
SW-0	115	0.221	ND	--	--	(0900-1130)
N-1	270	0.518	0.722	1.39	0.465	
SE-1	275	0.528	0.034	0.064	0.021	3/8/93
SW-1	275	0.528	0.027	0.051	0.017	(1230-1600)
N-2	865	1.66	4.36	2.63	0.880	
SE-2	865	1.66	10.6	6.39	2.14	
SW-2	865	1.66	20.6	12.4	4.15	3/8-9/93
B-2	--	--	ND	--	--	(1600-0600)
N-3	630	1.21	8.46	6.99	2.34	
SE-3	625	1.20	2.54	2.12	0.709	3/9/93
SW-3	625	1.20	290.	242.	81.0	(0600-1700)
N-4	815	1.56	110.	70.5	23.6	
SE-4	815	1.56	173.	111.	37.1	
SW-4	815	1.56	350.	224.	74.9	3/9-10/93
B-4	--	--	ND	--	--	(1700-0630)
N-5	290	0.557	12.3	22.1	7.39	
SE-5	290	0.557	58.4	105.	35.1	3/10/93
SW-5	290	0.557	43.3	77.7	26.0	(0630-1100)
N-6	330	0.634	3.69	5.82	1.95	
SE-6	330	0.634	97.0	153.	51.2	3/10/93
SW-6	330	0.634	14.7	23.2	7.76	(1100-1700)
N-7	950	1.82	36.7	20.2	6.76	
SE-7	945	1.81	39.5	21.8	7.29	3/10-11/93
SW-7	950	1.82	15.3	8.41	2.81	(1700-0830)
SP-11	1.0 ug Spike		0.699	--	--	
SP-12	1.0 ug Spike		0.724	--	--	
SP-13	1.0 ug Spike		0.690	--	--	
SP-14	1.0 ug Spike		0.678	--	--	

* All flows at 1.92 liters per minute.

$$\text{ppbv} = (\text{ug/m}^3) \times \frac{(8.21 \times 10^{-2} \text{ liter-atm/mole} \cdot ^\circ\text{K})(298^\circ\text{K})}{(73.12 \text{ gram/mole})(1 \text{ atm})}$$

ND = Not Detected, <0.075 ug/sample.

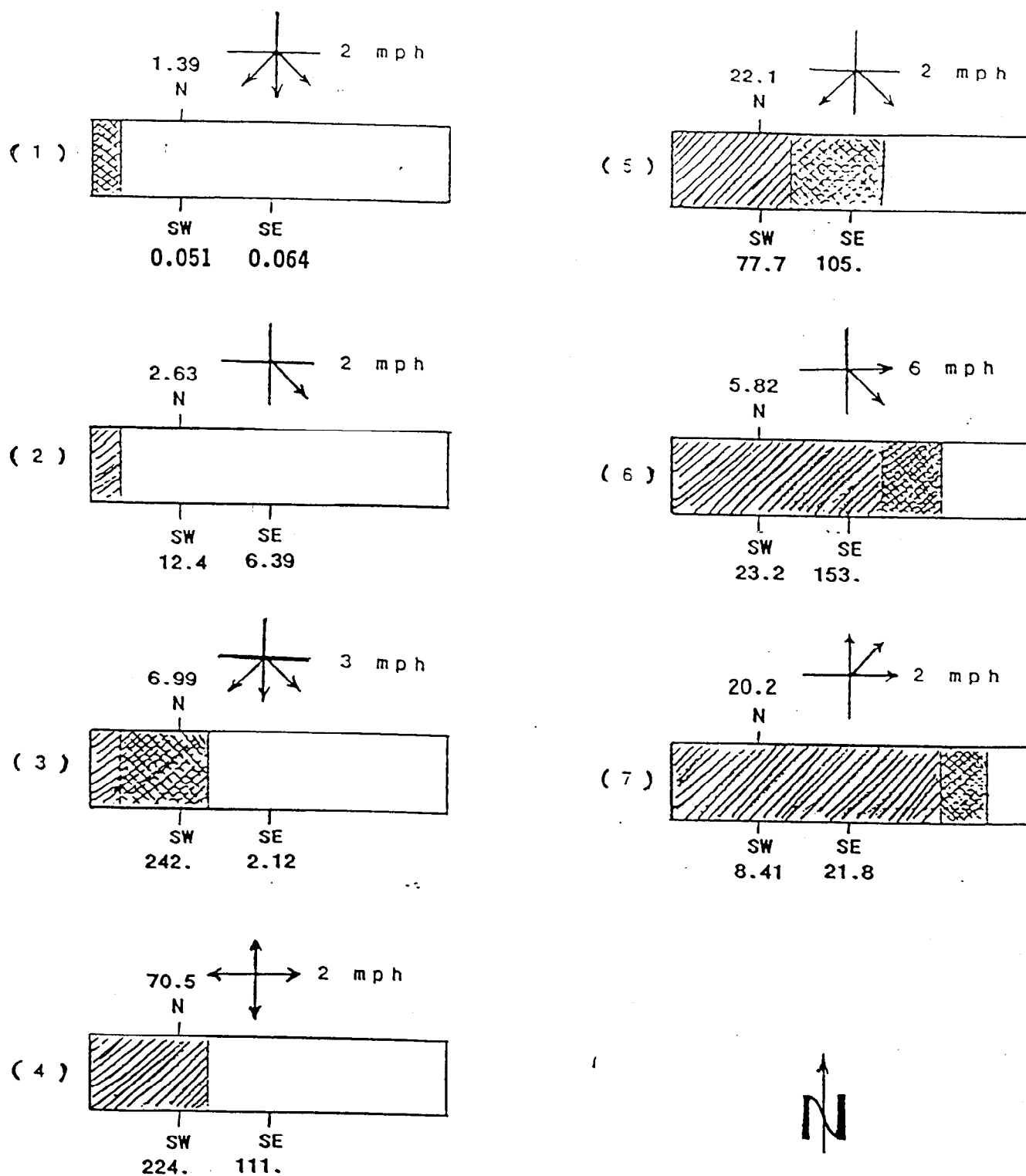
TABLE II. MITC Meteorological Data

Sampling Period	Wind Direction *	Wind Speed (mph)
0	N/S/E/W	1
1	NE/ N /NW	2
2	NW	2
3	NE/ N /NW	3
4	N/S/E/W	2
5	NE/NW	2
6	W/ NW	6
7	S/SW/W	2

BOLD indicates predominant wind direction, if any.

* Indicates direction wind blows from.

TABLE III. Summary of MITC Data ($\mu\text{g}/\text{m}^3$)



Legend	
	Already applied
	Applied during sampling period
()	indicates sampling period

Arrow indicates direction wind is blowing toward.
Wind speed is averaged for the entire sample period.

TABLE IV. MITC Quality Assurance Confirmation
Data, Total ug MITC Detected

Sample ID	AIHL GC/NPD	AIHL GC/MS	(%) ¹⁾	CDFA GC/NPD	(%) ¹⁾
N-2	4.36	3.63	(83)		
SE-2	10.6	9.91	(93)		
SW-2	20.6	24.9	(121)		
N-3	8.46			9.85	(116)
SW-3	290.			310.	(119)
N-4	110.	135.	(123)		
SE-4	173.	179.	(103)	174.	(101)
SW-4	350.	346.	(99)	325.	(93)
B-4	ND			ND	
N-5	12.3			14.3	(116)
SE-6	97.0			122.	(126)
QC-1 (1.0 ug)				0.95	
Blank				ND	
5ug Spike				4.20 ²⁾	
N-7	36.7			34.4	(94)
SE-7	39.5			42.6	(108)
SW-7	15.3			15.8	(103)

¹⁾ Indicates the percentage this value is of that determined by AIHL using GC/NPD.

²⁾ 5 ug ea. spiked in front, back and glass wool. This value is the average of all three.

ND = not detected: AIHL GC/NPD = <0.075 ug/sample, AIHL GC/MS = <0.038 ug/sample, CDFA GC/NPD = <0.20 ug/sample.

APPENDIX I.
SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE SAMPLING AND QA/QC MONITORING PROTOCOL

Sampling and Quality Assurance Procedures for the Monitoring of Certain
Breakdown Products of Metam Sodium in Imperial, Kern or
Contra Costa County during Fall 1992

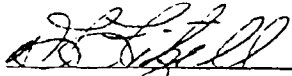
Engineering Evaluation Branch

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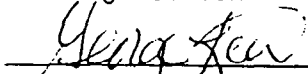
Project No. C92-070

Date: October 15, 1992

APPROVED:


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_____, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Sampling and Quality Assurance Procedures for the Monitoring of Certain
Breakdown Products of Metam Sodium in Imperial, Kern or
Contra Costa County during Fall 1992

I. Introduction

The Cal/EPA Office of Environmental Health Hazard Assessment (OEHHA) and the Department of Pesticide Regulation (DPR) have requested that the Air Resources Board (ARB) conduct ambient air monitoring for methyl isothiocyanate (MITC). MITC is the primary breakdown product of metam sodium (sodium-N-methyldithiocarbamate). MITC is responsible for the pesticidal activity of metam sodium. In response to this request, ARB staff will conduct a 3-day source impacted ambient monitoring program after an application of metam sodium, as well as an ambient monitoring program within populated areas. This monitoring will focus primarily on MITC, although limited monitoring for two other breakdown products, hydrogen sulfide and carbon disulfide will also be conducted.

An extensive Quality Assurance/Quality Control (QA/QC) program is planned to ensure the accuracy of the results (Attachment A). Because of the emergency nature of the Dunsmuir spill, it was not possible to implement full QA/QC procedures at that time. It is felt a thorough QA/QC program at this time will substantiate both studies.

Metam sodium is an herbicide, fungicide, insecticide and nematocide primarily used as a preplant fumigant. Its peak use in California is in Kern County during the months of July and August. Since metam sodium is used in various parts of the state, the monitoring location will be selected by ARB, DPR, OEHHA after identifying those areas with the peak metam sodium usage rate. DPR's "Monitoring Recommendation for Metam-sodium" is presented in Attachment B. Metam sodium is applied by soil injection or sprinkler irrigation. Results of the monitoring will be evaluated by staff of the OEHHA and the DPR.

II. Sampling

A sketch of the sampling apparatus is shown in Attachment C. The apparatus consists of a charcoal adsorbent tube, rain and light cover, rotometer, train support and vacuum pump. Charcoal adsorbent tubes will be used for the collection of MITC and carbon disulfide samples.

Hydrogen sulfide will also be monitored on site using a Jerome portable analyzer. This instrument measures hydrogen sulfide based upon its reaction with a gold film. The Jerome is hand-held and battery operated instrument capable of only providing instantaneous readings at one location. All results are real time and cannot be time averaged. This instrument has a detection limit of 3.0 ppb. Hydrogen sulfide will be monitored during the application monitoring and also the ambient monitoring, if feasible.

A. Application Monitoring

Air sampling will be coordinated with the appropriate County Office of the Agricultural Commissioner, and an applicator. Three samplers will be set

up: 1) approximately 15 yards upwind, 2) approximately 15 yards downwind and 3) approximately 150 yards downwind of the field. Prior to application, background samples will be taken to establish if any MITC is detectable. A meteorological station will also be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. A log book will be kept with information on the field size, application rate, formulation, length of application and any other pertinent information.

Ambient air will be pulled through the sampling tubes at a flow rate of approximately 2 liters per minute using battery powered pumps. Duplicate samples will be collected from each sampler for quality assurance purposes. The sampling schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (Attachment D) will be followed as closely as practical. Based on the laboratory detection limit of $0.2 \mu\text{g}/\text{sample}$, the detection limits will range (approximately) from $1.67 \mu\text{g}/\text{m}^3$ for the one hour background sample to $0.07 \mu\text{g}/\text{m}^3$ for the 24-hour samples.

B. Ambient Monitoring

Three to five samplers will be set up at various locations throughout the County. Sampling sites will be selected based upon criteria outlined in the "Quality Assurance Plan for Pesticide Monitoring" and will be in population centers near application sites where public exposure may occur if the levels are significant. The samplers will be powered by 115VAC vacuum pumps.

Twenty-four hour samples will be taken Monday through Friday at a flow rate of approximately 4 liters/minute. Based on the laboratory detection limit of $0.2 \mu\text{g}/\text{sample}$, the detection limit for the ambient samples will be (approximately) $0.03 \mu\text{g}/\text{m}^3$.

III. Analysis

All samples will be stored in an ice chest or freezer until analysis. Analysis of MITC samples will be performed by the Department of Health Services Air and Industrial Hygiene Laboratory. The analytical method is extraction with carbon disulfide, separation by gas chromatography using a DB-624 column and measurement by a nitrogen/phosphorus detector. The analytical procedure is described in Attachment E and Attachment F.

At this time it is anticipated that some of the duplicate samples from both the ambient and the application monitoring will be sent to ICI (formerly Stauffer) for carbon disulfide analysis. Detection limit for this compound is 0.3 ppb. A copy of ICI's analytical procedure for carbon disulfide can be found in Attachment G.

IV. Quality Assurance

Calibrated rotometers will be used to control sample flow rates. Sampler flow rates will be calibrated prior to and after sampling in the field. Samplers will be leak checked with the sampling media installed prior to and after each sampling period. A field log book will be used to record sample start and stop

times, duration of the application, sample IDs, any change in the flow rates, and other pertinent information. A chain of custody sheet will accompany all samples.

The dependent parameters (reproducibility, linearity and minimum detection limit) of the analytical instrument will be checked prior to analysis. A laboratory audit will be conducted prior to sampling in order to review methods and establish the accuracy of the methods through the use of spiked samples. This audit program will be developed by the ARB, DPR, and laboratory staff. Blank sampling tubes will accompany each batch of samples from the field to the lab prior to analysis. Trip spikes will also be prepared by ARB's Quality Management and Operations Support Branch (QMOSB).

Method development procedures to document the performance of the sampling/analytical methodology were previously conducted. Methods development data are presented in Attachment F.

V. Personnel

ARB Monitoring personnel will consist of Don Fitzell (Project Engineer) and Jack Rogers (Instrument Technician).